On the Thermodynamic Consistency of the Temperature Dependence of the Debye Temperature

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If the Debye temperature (Θ) has temperature dependence, then the expression for lattice heat capacity at constant volume is

$$C^* = C / 3\, N_A\, n\, k_b = (C_D / 3\, N_A\, n\, k_b)\, [1 \text{ ñ } (T/\Theta)(d\,\Theta / d\,T)_v\,]^2 \text{ ñ}$$

$$\text{ñ } [\,(3/8) + (T/\Theta)\, D(\Theta/T)]\, T\, (d^2\,\Theta / d\,T^2\,)_v. \qquad (1)$$

Here, N_A is the Avogadro number, n is the number of ions in molecule, k_b is the Boltzmann constant, D(x) is the Debye function, which have form

$$D(x) = (3/x^3)\int_0^x \{\, t^3 / [\exp(t) \text{ ñ } 1]\}\, dt,$$

$$C_D / 3\, N_A\, n\, k_b = 4\, D(\Theta/T) \text{ ñ } 3(\Theta/T) / [\exp(\Theta/T) \text{ ñ } 1] \;.$$

When the temperature tends to zero the function (1) must smoothly decrease to zero (it is the third law of thermodynamics). This condition requires that the dependence of $\Theta(T)$ satisfy the demands: the low-temperature branch of $\Theta(T)$ at $0 \le T \le \Theta$ must vary with T as

$$\Theta(T)_{low} \cong \Theta_0\, [\,1 \text{ ñ } \chi\,(T/\Theta_0)^k\,] \quad , \text{ where: } \Theta_0 = \lim_{T \to 0K} \Theta(T) \;;\; \chi \ge 0 \;;\; k \ge 4 \;. \qquad (2)$$

At high temperature, the function (1) must increase, tending at $T/\Theta \to \infty$ to dependence

$$C^*_{high} \cong [1 \text{ ñ } (1/20)(\Theta/T)^2]\, [1 \text{ ñ } (T/\Theta)(d\,\Theta / d\,T)_v\,]^2 \text{ ñ } (T^2/\Theta)(d^2\,\Theta / d\,T^2)_v \;.$$

This leads to the next form of high temperature branch of $\Theta(T)$

$$\Theta(T)_{high} \cong \Theta_\infty \exp(\text{ ñ } \alpha\, \Theta_\infty / T)\,, \quad \text{ where: } \Theta_\infty = \lim_{T/\Theta_\infty \to \infty} \Theta(T) \;;\; \alpha \ge 0\,. \qquad (3)$$

Value α is a fitting parameter. The unification of the low temperature branch (2) with the high temperature branch (3) leads to the function $\Theta(T)$ that can be employed at all temperature intervals

$$\Theta(T) = \Theta_0 \exp[\text{ ñ } \chi\,(T/\Theta_0)^k\,] + \Theta_\infty \exp(\text{ ñ } \alpha\, \Theta_\infty / T) \qquad (4)$$

Thus, the function $\Theta(T)$ smoothly decreases from Θ_0 (at T = 0 K) to a minimum, and then it smoothly increases, tending to an asymptotic value Θ_∞ at $T/\Theta \to \infty$. For calculation of function $\Theta(T)$ it is necessary to define of the five parameters: Θ_0, χ, k, Θ_∞, α. In this way, function $\Theta(T)$ doesn't lead to results that contradict the laws of thermodynamics.

The values of Θ_0 and Θ_∞ are defined for many materials and are in handbooks. A method for the definition of other parameters: χ, k, α by means of experimental data is proposed. It is shown that for simple monatomic materials at $T \approx 0$ K, $k \cong 4$.